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## Analysis of Ethane and Diethylbenzene Bridged Sorbents

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## **EXECUTIVE SUMMARY**

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) has evaluated samples provided by Aurora Analytics, LLC (Baltimore, MD). Three types of samples were evaluated. The first two were synthesized following the NRL developed protocol for synthesis with and without slight modifications for production of hierarchical organosilicate sorbents containing mixed ethane and diethylbenzene bridging groups at the one gram scale. A third set of materials was produced using a modification of this protocol to synthesize a batch of sorbent at ten times the original scale. Materials were evaluated by nitrogen adsorption, thermogravimetric analysis, and based on analysis of target capture. The results were compared with those obtained for an NRL-synthesized sorbent material.



# ANALYSIS OF ETHANE AND DIETHYLBENZENE BRIDGED SORBENTS

## INTRODUCTION

Under an agreement to provide articles and services (NRL-2017-014), the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) evaluated sorbent materials produced by Aurora Analytics on behalf of Grey Matter. These materials are the result of Grey Matter's ongoing efforts related to licensing agreements for NRL patent US 7,754,145 B2 and NRL patent application US 14/209728. Materials were synthesized based on the published protocol for production of hierarchical sorbent materials comprised of mixed ethane and diethylbenzene bridging groups. [1] This class of materials has been applied by NRL to capture and retention of nerve agent simulants [1] with variations on the sorbent applicable to a wide range of other targets. [1 - 20] The basic protocol reproduced by Aurora Analytics has also been used to generate coatings on solid surfaces and on textiles by NRL. Textiles modified in this manner have been shown to reduce or eliminate transport of chemical warfare agents and simulants across the fabric barrier. Modification of the hierarchical sorbents using a porphyrin has been shown to impart catalytic activity to the sorbents, providing the potential for an active barrier material that both sequesters and eliminates threat agents. [4, 20]

The current document summarizes results for analysis of the sorbent materials produced by Aurora Analytics. An initial set of sorbents received by NRL were synthesized either through following NRL's protocol or through a modification to the protocol at the stage of addition and mixing. A follow-on process produced materials using this modification to synthesize a batch of sorbent at ten times the original scale. Materials were evaluated by nitrogen adsorption, thermogravimetric analysis, and based on analysis of target capture. The results were compared with NRL-synthesized sorbent material.

## PROTOCOL

The protocol for sorbent synthesis provided to Aurora Analytics was that published by Melde, *et al.* in 2010. [15] This procedure calls for Pluronic® P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), average Mn ~5,800, CAS 9003-11-6); 1,3,5-trimethylbenzene (TMB, FW 120.19); nitric acid (70%, FW 63.01) used to prepare a 0.1 M HNO<sub>3</sub> solution in water; hydrochloric acid (37%, FW 36.46); deionized water (18.2 MΩ-cm, FW 18.02); ethanol (200 proof, FW 46.07); 1,2-bis(trimethoxysilyl)ethane (BTME, FW 270.43, CAS 18406-41-2); and bis(trimethoxysilyl)ethylbenzene (DEB, FW 374.58, CAS 58298-01-4). On discussion with NRL, Aurora Analytics replaced the original DEB with CAS 266317-71-9.

Pluronic P123 (1.9 g) is dissolved with TMB (0.55 g) in 0.1 M HNO<sub>3</sub> (7.5 g) using a closed reactor at 60°C with constant stirring. The mixture is cooled to room temperature and a mixture of the silanes is added dropwise to achieve even dispersion. The silane mixture is comprised of BTME (1.06 g) and DEB (1.47 g). The reaction is stirred for an additional minute to ensure homogeneity. The mixture is then transferred to a culture tube, an air tight seal is applied, and it is heated at 60°C for ~18h. During this time a white gel will form. The tube is then unsealed and heated for an additional 2 d at 60°C followed by 80°C for 2 d. This product, a white monolith, is then refluxed in a solution of 1 M HCl in ethanol for ~18 h to extract the surfactant. The concentration of HCl is not exact in this step and adjustments would be expected



under a commercial scale procedure. The material is collected by vacuum filtration, and reflux is repeated with a fresh HCl solution two additional times. The monolith is broken into particles or powder during this process. The final collected product is rinsed with fresh ethanol (~500 mL) and water (~1 L) and dried at  $>100^{\circ}\text{C}$ .

## RESULTS

Morphological characteristics were determined for the Grey Matter and NRL sorbents using standard nitrogen adsorption assessments. Nitrogen adsorption-desorption analysis was performed on a TriStar II Plus porosimeter at 77 K (Micromeritics Instrument Corporation, Norcross, GA, USA). Samples were degassed to 1  $\mu\text{m}$  Hg at  $100^{\circ}\text{C}$  prior to sorption analysis. Surface area was calculated by the Brunauer-Emmett-Teller (BET) method, pore size by the Barrett-Joyner-Halenda (BJH) method, and total pore volume by the single point method at relative pressure ( $P/P_0$ ) 0.97. Results are summarized in Table 1. Figure 1 shows the results of nitrogen adsorption/desorption analysis for the four sorbents. GM-003 shows significant increases in hysteresis over the NRL sorbent. Type IV / type I isotherms of the type shown here are common to these mesoporous materials. The pore size distribution for GM-003 is wider than that of the NRL sorbent and indicates significantly larger pores. The GM-004 sorbent, on the other hand, shows behaviors and morphological characteristics that are more closely related to that of the NRL material.

Table 1 – Morphological Characteristics

Sample	Surface Area ( $\text{m}^2/\text{g}$ )	Pore Volume ( $\text{cm}^3/\text{g}$ )	Pore Size ( $\text{\AA}$ )
NRL Sorbent	694	0.72	65
Lot GM-003	511	0.59	87
Lot GM-004	560	0.61	75
Lot GM-005	596	0.77	75

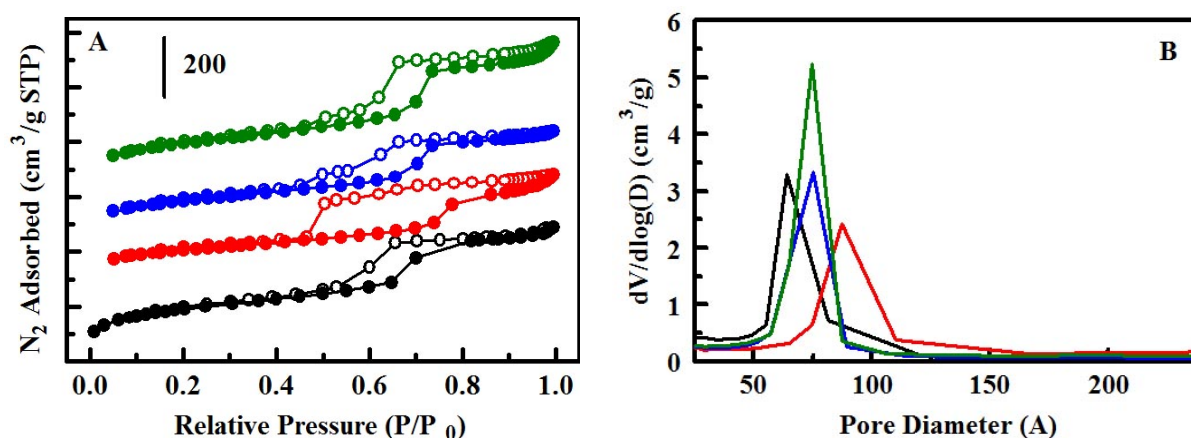


Fig. 1 — Nitrogen adsorption assessment. (A) Nitrogen adsorption/desorption for the NRL sorbent (black) [15] and the Grey Matter sorbents, GM-003 (red), GM-004 (blue), and GM-005 (green). (B) Pore size distribution for the sorbents, colors as in panel A.

Thermogravimetric analysis was performed using a TA Instruments Hi-Res 2950 Thermogravimetric Analyzer under a N<sub>2</sub> atmosphere; temperature was ramped 5°C/min to 800°C. This process is used to verify the removal of surfactant from the product. The surfactant is responsible for templating the pore structure of the sorbents. Removal of surfactant is necessary to free the pore voids, allowing for target uptake in an application. Both TGA analysis and the results of nitrogen adsorption/desorption indicate effective removal of surfactant from the product.

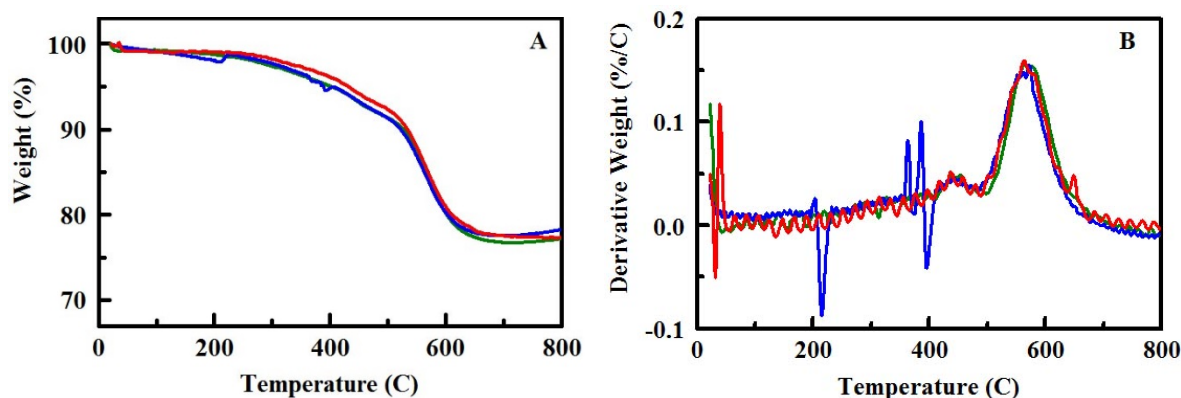


Fig. 2 — Thermogravimetric analysis. (A) Weight percent analysis for the Grey Matter sorbents, GM-003 (red), GM-004 (blue), and GM-005 (green). (B) Data presented based on derivative weight, colored as in panel A.

Batch type experiments were used to characterize the binding capacity and affinity of the sorbent materials. Experiments were conducted in 20 mL scintillation vials (EPA Level 3; clear borosilicate glass; PTFE/silicone-lined cap) using a fixed mass of sorbent between 5 and 35 mg. Target samples were prepared in 18.2 MΩ Milli-Q deionized water at concentrations between 20 and 40 ppm. Target solutions (20 mL) were added to the sorbents in the vials with a portion of the solution retained for use as a control during chromatographic analysis. Vials were incubated overnight on rotisserie mixers. Samples were filtered using 25 mm Acrodisc 0.2 μm syringe filters with PTFE membranes prior to processing and analysis. Difference method analysis was applied to determine the target removed from solution.

For paraoxon analysis, a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC; 40 μL injection volume) coupled to a photodiode array detector (SPD-M20A; 277 nm) was used. The stationary phase was a C18 stainless steel analytical column (Luna, 150 mm x 4.6 mm, 3 μm diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min). [21] A series of dilutions was used to produce a standard curve for comparison, and aliquots of stock solutions were measured. Variations in the calibration curves were typical at ±5%.

Figure 3 presents the data collected for target binding by the sorbent materials. For the conditions established above (5 to 35 mg sorbent in 20 mL of 20 to 40 ppm paraoxon), the sorbents bind nearly all of the target from the solutions.

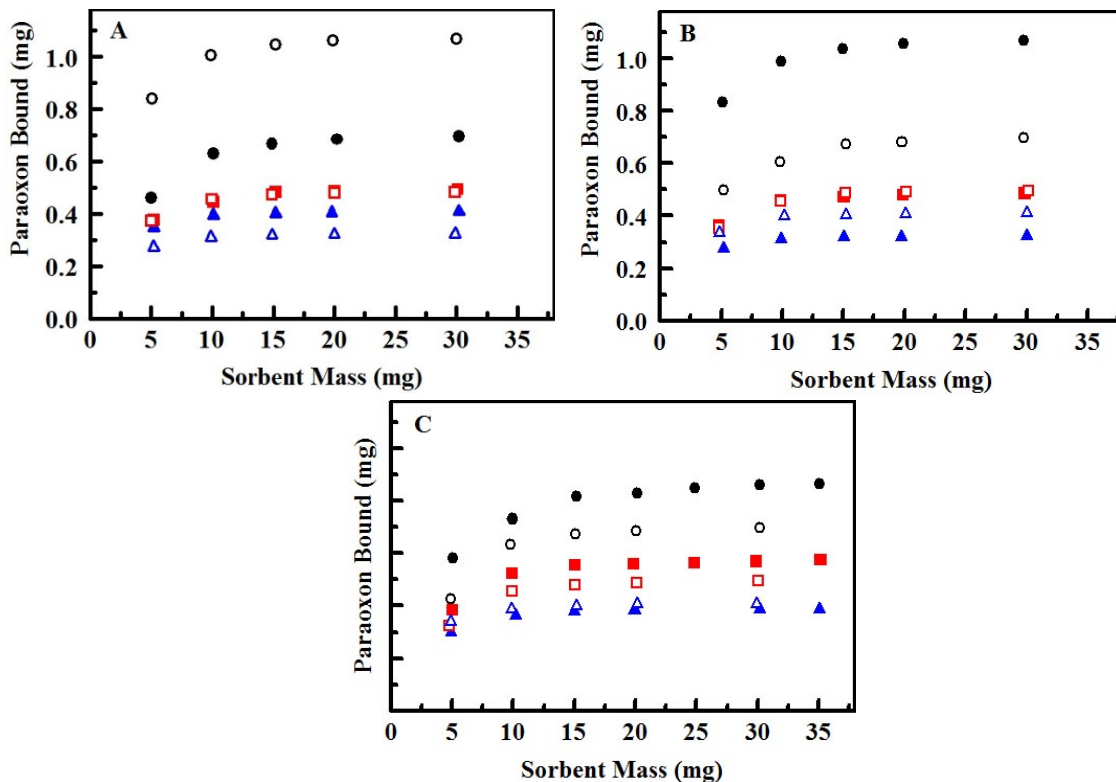


Fig. 3 — Target capture by the Grey Matter sorbents: (A) GM-003; (B) GM-004; (C) GM-005.

We have previously applied the Langmuir-Freundlich (LF) isotherm for describing target binding by sorbents of this type. [6, 7] The limited water solubility of paraoxon (3.6 g/L) and similar targets (diazinon 0.07 g/L) result in different behavior for these sorbents. Binding isotherms for these compounds do not indicate formation of a target monolayer on the sorbent surface, the behavior described by the LF isotherm. Estimates of target volume adsorbed in the original NRL experiments indicated that the targets were approximately filling the available mesopore void volume. [1] This behavior is a capillary-phase separation type of interaction and is more appropriately described by the Freundlich-BET expression:

$$q = kL^n + \frac{\frac{\alpha}{m}k_sSL}{(S-L)(S+(k_2-1)L)}$$

where  $q$  is the amount of target bound per unit sorbent surface area,  $L$  is the free ligand,  $S$  is the target solubility,  $k$  and  $k_2$  are the affinity coefficients,  $n$  is a heterogeneity coefficient, and  $m$  is the mass. Here,  $\alpha$  divided by the mass ( $m$ ) yields the saturation capacity typically utilized in this model,  $q_s$ . This expression was applied to the data sets on paraoxon binding collected for the Grey Matter sorbents. Figure 4 presents the isotherms generated for the materials on the basis of this approach. Results for the NRL sorbent are included for comparison. Table 2 provides a summary of the determined parameters.

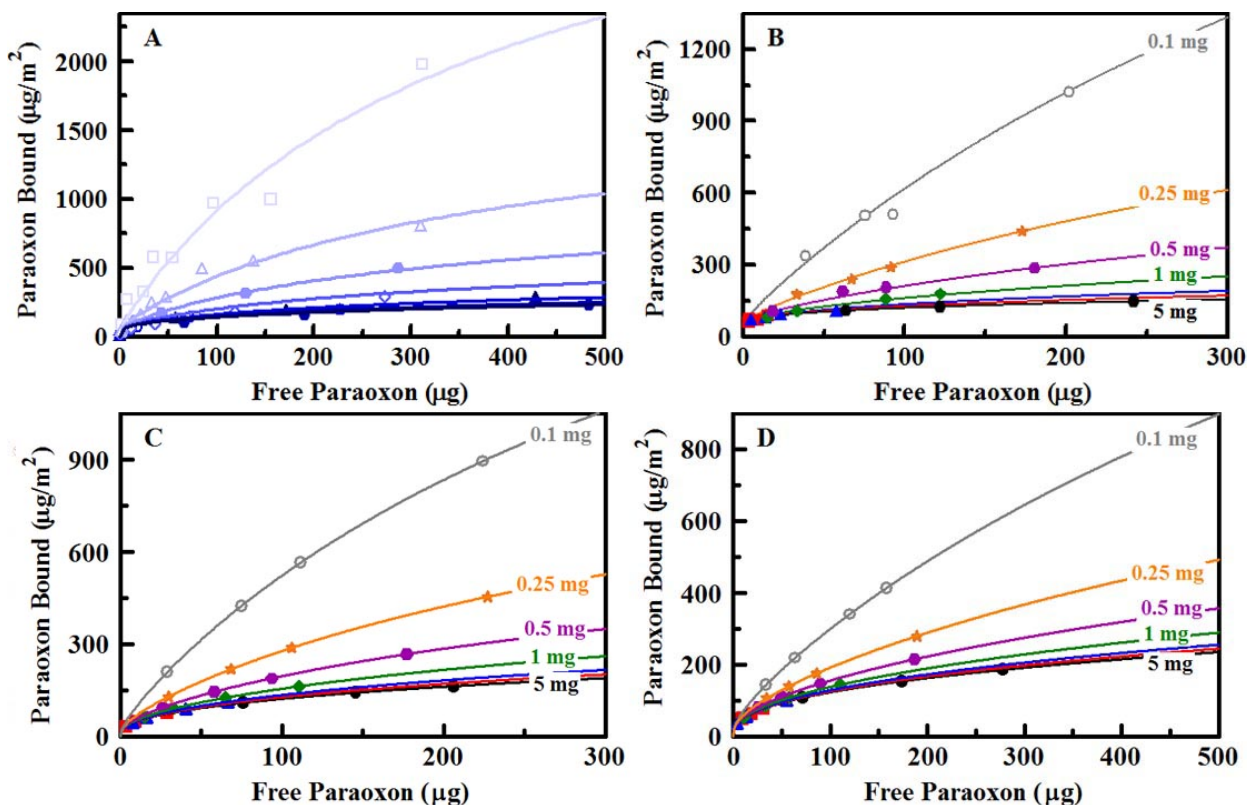


Fig. 4 — Target capture by the sorbents and associated Freundlich-BET isotherms: (A) NRL sorbent [15]; (B) GM-003; (C) GM-004; (D) GM-005.

Table 2 – Freundlich-BET fitting parameters

Sample	$\alpha$ ( $\mu\text{g}/\text{m}^2 \text{ g}$ )	$k$ ( $\mu\text{g}^{-1}$ )	$k_2$	$n$	$S$ ( $\mu\text{g}$ )
NRL Sorbent	0.14	21	17	0.36	72,000
Lot GM-003	0.37	52	115	0.16	72,000
Lot GM-004	0.21	21	173	0.37	72,000
Lot GM-005	0.21	21	67	0.38	72,000

## CONCLUSIONS

The study summarized here addresses assessment of samples produced for Grey Matter (Rockville, MD) by Aurora Analytics, LLC (Baltimore, MD). An initial set of sorbents received by NRL were synthesized either through following NRL's protocol or through a modification to the protocol at the stage of addition and mixing. A follow-on process produced materials using this modification to synthesize a batch of sorbent at ten times the original scale. Materials were evaluated by nitrogen adsorption, thermogravimetric analysis, and based on analysis of target capture with results compared to NRL-synthesized sorbent material. Results for nitrogen adsorption showed significant hysteresis for the Aurora material synthesized without modifications. The pore size distribution was also wider than that of the NRL sorbent and indicated significantly larger pores. The modified synthesis showed morphological

characteristics that were more closely related to that of the NRL material. The larger scale production (10x) showed morphological characteristics very similar to those of the smaller production scale. Adsorption of targets by the sorbents followed the behaviors observed for the NRL materials including the noted capillary-phase separation. Binding affinities were slightly less for the Aurora materials while saturation capacities were slightly higher.

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